

Dredging Research

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Measurement and Prediction of Volatile Emissions from Contaminated Sediments in Confined Disposal Facilities

by Cynthia Price, Environmental Laboratory, ERDC-WES

Placement of contaminated dredged material into a confined disposal facility (CDF) is one of several alternatives available to managers when working on dredging projects. However, this type of disposal may involve the emission of contaminants from sediments. There are actually several contaminant migration pathways from CDFs. Paths include effluent discharges to surface water, rainfall surface runoff, leachate into groundwater, volatilization to the atmosphere, and direct uptake by plants and animals. Research, funded under the Long Term Effects of Dredging Operations (LEDO) program, is presently under way to evaluate volatile emissions from contaminated sediments.

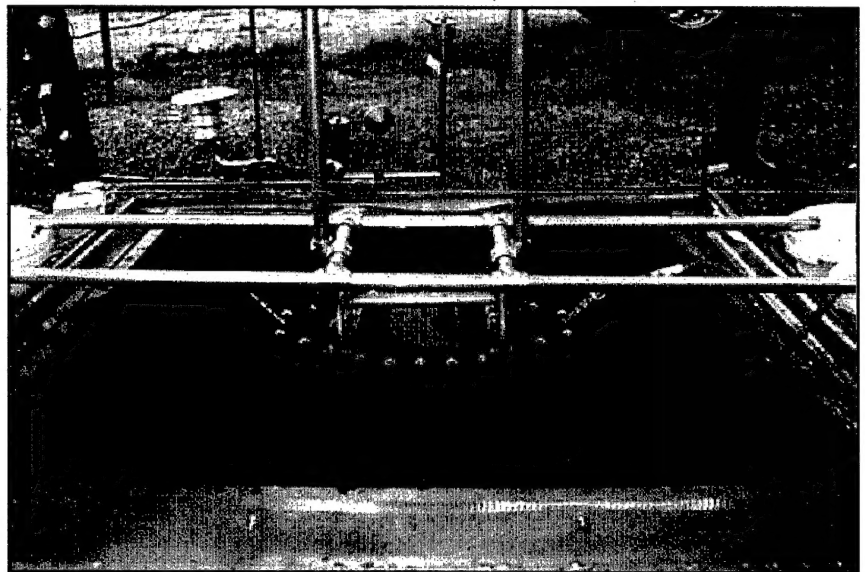
Emissions of volatile organic compounds (VOCs) depend on a variety of factors: sediment physical characteristics, such as aging, porosity, moisture content, and percent oil and grease; contaminant chemical properties, for example Henry's Law Constant and vapor pressure; and environmental vari-

ables such as relative humidity and temperature. Dredging, disposal, and placement operations in CDFs can increase the potential for emissions of these compounds from exposed contaminated sediments. Methods for predicting volatile losses are needed in order to develop guidelines for controlling emissions from contaminated dredged materials.



Background

Initial research efforts focused on modifying an existing laboratory apparatus to measure volatile emissions. The design resulted in a chamber, constructed of two pieces of anodized aluminum, with a well



Field flux chamber

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to hold a 2.54-cm-deep sediment layer on a 30-cm² surface area. Experiments measured VOC emissions from Rouge River, Michigan, sediment, and these experiments found that the release of VOCs was affected by the flow rate of air passed over the sediment's surface.

Due to the limitations of this small chamber, a larger chamber was designed and constructed by Louisiana State University (LSU) and ERDC personnel. The new chamber size increased the bottom portion to hold a 10-cm sediment depth with a 375-cm² surface area. The top portion was designed with channels to evenly distribute air flow across the sediment surface. The chamber was sealed with an O-ring and threaded fasteners for an air-tight fit (Fig. 1). After testing the large chamber, laboratory investigations were designed to measure air emissions rates of VOCs under a variety of environmental conditions. Mathematical models generated by the LSU Department of Chemical Engineering using data generated from experiments conducted at the ERDC and LSU estimated air emission rates of the VOCs.

Experiments

Emissions from three naturally contaminated field sediments and one laboratory-spiked sediment were investigated to formulate comparisons of contaminant fluxes between these two types of sediments. The University Lake (UL), Baton Rouge, La., was the source of the laboratory-spiked sediment. Field sediments were obtained from three sites that are scheduled for dredging and CDF disposal by the Corps: the Indiana Harbor Canal (IHC), the Grand Calumet River (GCR), and New York Harbor (NYH). The experiments provided data on contaminant fluxes under different air humidity, sediment moisture, and site management conditions that may occur during CDF operations. Selected polyaromatic hydrocarbon (PAH) compounds were chosen as representative VOCs

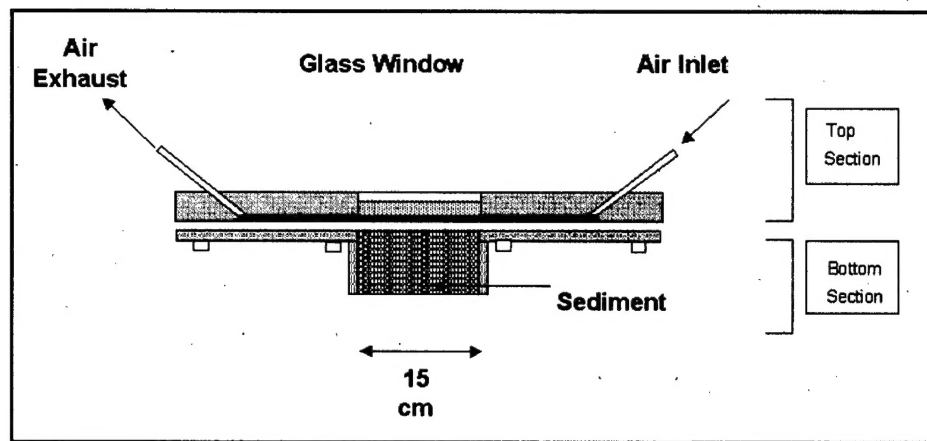


Figure 1. Laboratory flux chamber

due to their prevalence in contaminated sediments (Fig. 2). Additional VOC emissions were measured according to each sediment's contaminant loading, including polychlorinated biphenyls (PCBs), pesticides, dioxins, ammonia, hydrogen sulfide, and methyl mercaptans.

During the experiments, flux chambers were filled with a known weight (wet weight, approximately 2,100 grams) of sediment and sealed. Air was passed over the sediment surface at 1.7 L/min while relative humidity was maintained using an in-line bubble trap. Commercially available contaminant-specific, absorbent-filled air sampling traps were attached to the chamber exit ports.

Sampling schedules differed for each sediment, dependent upon the environmental conditions tested. Sampling of IHC, GCR, and NYH sediments consisted of continuous runs, with alternating sediment moisture and relative air humidity conditions. The IHC and GCR sediments were then reworked,

and emissions were measured to evaluate the effects of sediment disturbance.

Contaminant flux, $N(t)$, through the chambers was calculated using the equation

$$N(t) = \Delta m / \Delta t A_c$$

where

Δm = mass (ng) of compound collected on the trap in time Δt (hr)

A_c = area of the sediment-air interface, cm²

Experimental Results

For model development, data from several laboratory experiments were collected on sediment-to-air fluxes of VOCs. The following are experimental results from laboratory and field investigations conducted at the ERDC and model development conducted at LSU:

➤ **Contaminant Fluxes:** Figure 3 shows emissions of phenanthrene

Contaminant	IHC	GCR	NYH	UL
Naphthalene (mg/kg)	38	586	0.2	na*
Phenanthrene (mg/kg)	51	432	0.9	97
Pyrene (mg/kg)	59	172	1.9	94
Oil and grease (%)	1.0	1.4	0.03	0
* na (sample was not spiked with naphthalene).				

Figure 2. Contaminant loading of sediments

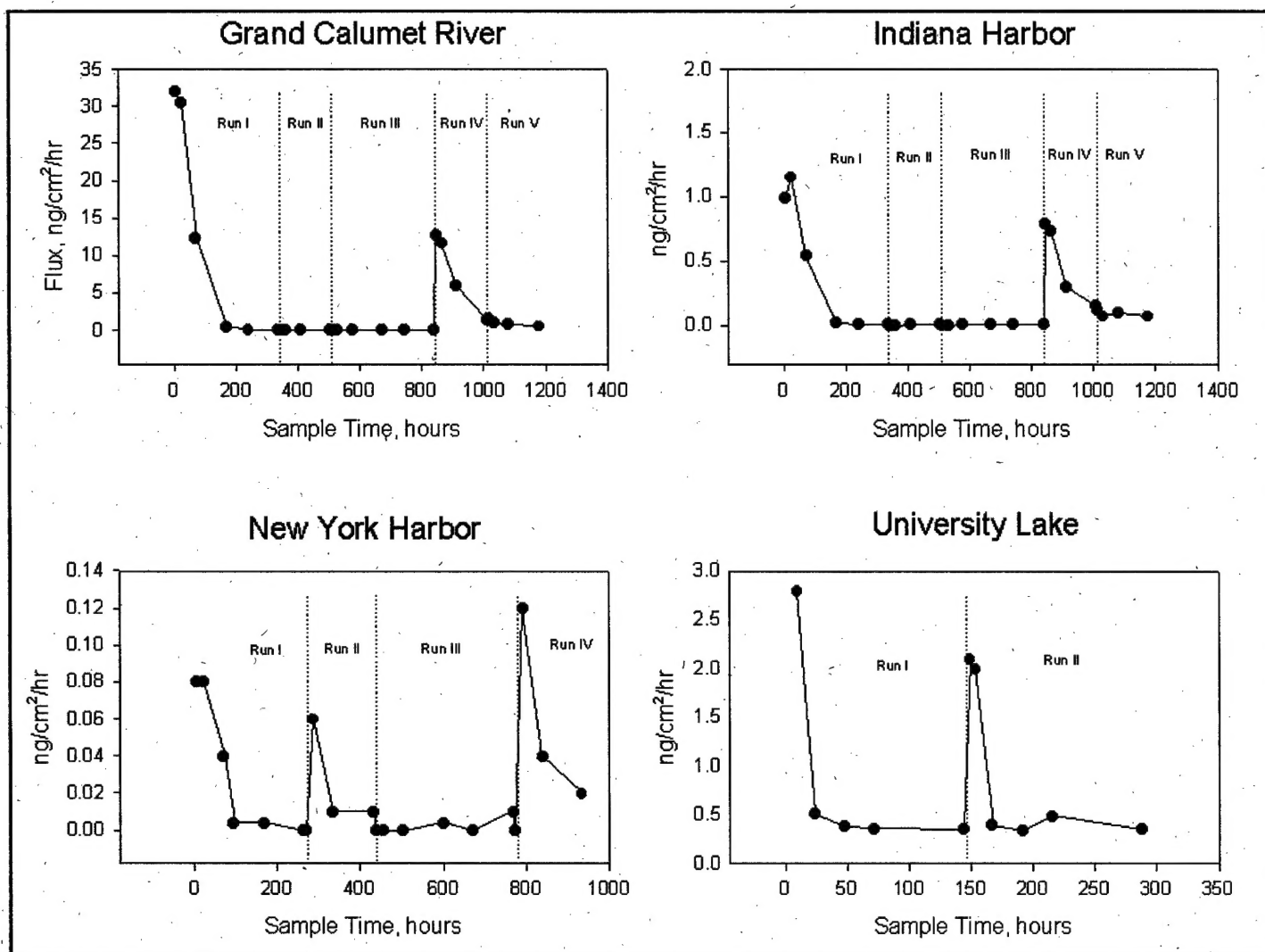


Figure 3. Phenanthrene fluxes from each sediment

over the course of laboratory investigations for each sediment.

➤ **Initial Placement:** Hydrocarbon fluxes exhibited sharp decreases in the first 24 to 48 hours after passage of dry air over the sediment surface (Run I) (Fig.3). As the sediment surface dried, flux decreased to low levels. These flux trends are characteristic for the majority of PAH compounds and are indicative of a diffusive transport of the contaminants from sediment to air.

➤ **Relative Air Humidity:** Increasing the relative humidity of air passed over the sediments showed varied results (Run II) (Fig.3). In the IHC and GCR sediments, which contained oil and grease, hydrocarbon

fluxes did not increase. The sorptive phase of oil and grease formed a thin oil film on the sediment surface from which the oil and contaminants evaporated. Subsequent diffusion through this oil layer would be much slower than through the pore air spaces. When humid air was passed over the two sediments which did not contain oil and grease (NYH, UL), contaminant fluxes increased (Run II) (Fig.3). This indicates decreased sediment sorptive capacity as a result of humid air, resulting in increased contaminant flux to air.

➤ **Rain Event:** Rewetting of a sediment decreases the sorptive capacity for contaminants and should theo-

retically produce increased fluxes. However, increasing sediment moisture in the IHC and GCR sediments to near field capacity (Run III) did not result in increased emissions. Moisture flux from these two sediments did not decrease over the course of the study, which would account for the lack of increased flux upon rewetting. Rewetting the NYH sediment (Run III) did not result in increased fluxes when humid air was passed over the sediment, but when dry air was applied (Run IV), emissions increased. This indicates decreased sediment sorptive capacity.

➤ **Sediment Disturbance:** Reworking the IHC and GCR sediments

brought underlying material to the surface, providing a new source of contaminant. This resulted in significant flux and emissions increases (Run IV) (Fig.3). Quick evaporation of the reformed oil layer could account for the observed flux, but once fluxes decreased, emissions would diffuse through the oil layer at a slower rate. A second addition of humid air (Run V) did not result in increased fluxes, verifying results found in Run II.

Verification of Results

A controlled field simulation experiment was conducted with IHC sediment to verify laboratory results. Volatile emissions were measured using a modified version of the VOC flux chamber (see cover). The chamber was designed to sample the same surface area as the laboratory apparatus. The bottom portion was open and fitted with knife-edge side panels which allow the chamber to be pushed into the sediment and form a seal over the surface. The field site consisted of a 4- by 4- by 2-ft-deep wooden chamber buried in the ground and filled with sediment. PAH emissions measurements were made over a 3-month period. The chamber was moved to different sections of the lysimeter in order to randomly sample the 16-ft² surface.

PAH fluxes in the field simulation showed behavior similar to that of the laboratory investigations. Fluxes decreased to a low concentration within the first 3 days of sampling. Rewetting of the sediment via a portable rainfall simulator did not result in increased fluxes.

The model prediction for phenanthrene, as outlined in the ADDAMS

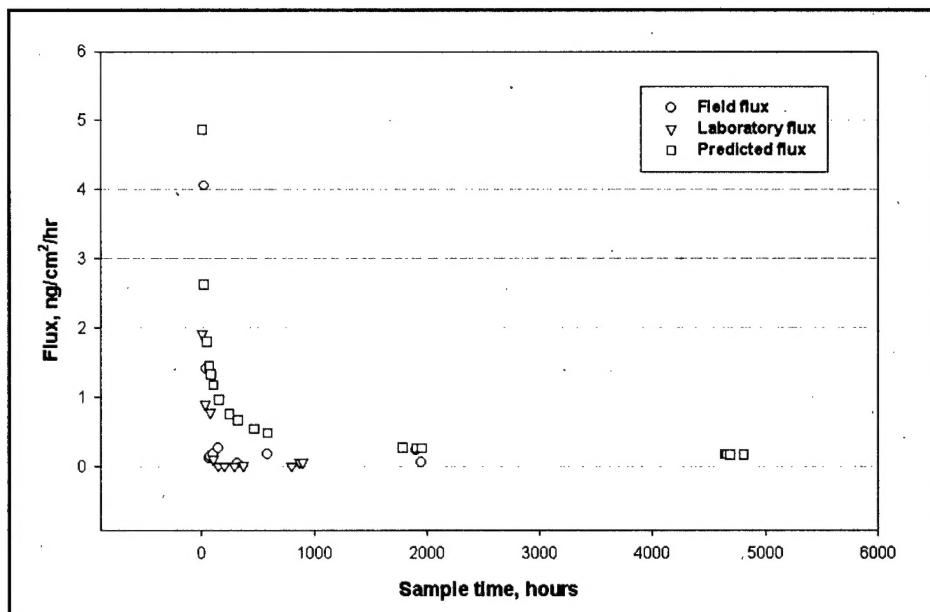


Figure 4. Experimental data (field simulation and laboratory) versus model for phenanthrene flux

suite of models (soon to be available at <http://www.wes.army.mil/el/elmodels/index.html#addams>) is compared to both the field and laboratory experimental data in Figure 4. Under all three scenarios, fluxes fell to below 1 ng/cm²/hr in the first few days after placement.

Conclusions

These investigations revealed that the highest contaminant fluxes occurred during the initial loading or placement stages (0-48 hr); followed by decreasing fluxes to low levels. Emissions also increased after mechanical mixing of the sediment. Contaminant fluxes were influenced by the additional sorptive phase of oil and grease, which appeared to prevent increased volatile emissions when moisture or relative air humidity was increased. In sediments not containing significant quantities of oil and grease, volatile emissions were

shown to increase under the above conditions. Contaminant emissions measured in the laboratory and field simulations agreed well with model predictions. The model, provided in ADDAMS, can be used to generate initial screening data for contaminant fluxes from freshly deposited dredged material.

Ongoing Investigations

Experiments are currently being conducted to obtain data on the emissions of VOCs from sediments resuspended in the water column. Various resuspension rates will be investigated to mimic different types of dredging equipment. This information will help select dredging devices that reduce the movement of contaminants into the water and air near dredging sites. These data are coupled with area air source dispersion models to yield concentrations of VOCs for exposure evaluation.

Additional information is available from Cynthia Price at pricec@wes.army.mil or Dr. Kaliat Valsaraj with the Department of Chemical Engineering at LSU at valsaraj@che.lsu.edu.

Assessment of contaminated dredged material for bioreclamation using genetic, biochemical, and physiological assays

by Dr. Edward Perkins, Environmental Laboratory, ERDC-WES

In the course of maintaining and improving navigation in waters of the United States, the U.S. Army Corps of Engineers must handle about 300 million cubic meters of dredged material annually. Five to ten percent of this material cannot be disposed of in open water due to contamination. Material not suitable for open-water disposal can be placed in confined disposal facilities (CDFs). Most CDFs, however, are at or are approaching capacity with new CDF sites difficult to find. Therefore, other means of disposal are needed.

Bioreclamation offers a potentially effective and affordable means of decontamination.

Once physical and chemical analyses indicate open-water disposal cannot be used, appropriate bioreclamation technologies are selected and tested. Many biotreatment alternatives are inexpensive and require minimal sample handling. However, successful application of bioreclamation requires knowledge of physiochemical and biological factors, limiting contaminant removal. These factors often vary from site to site.

Bioreclamation strategies are based upon stimulating microorganisms present in the dredged sediment to degrade pollutants. The generally unknown nature of microorganisms found in sediments can hamper selection and testing of bioreclamation strategies. Screening protocols have been developed at the ERDC-WES, Environmental Laboratory, to determine the types of microorganisms, the presence of key degradative bacteria, and the ability of a sediment to remove contaminants. These assays provide a basis for choosing appropriate biotreatments and for monitoring future progress and success of these systems.

More information is available from Dr. Perkins at (601) 634-2872, Fax: (601) 634-2839, e-mail: perkine@wes.army.mil, who performed this research in collaboration with Mr. David Ringelberg and Dr. Herbert Fredrickson under the Dredging Operations and Environmental Research Program. Related information is available from the Web site <http://www.wes.army.mil/el/dots/doer/technotes.html>

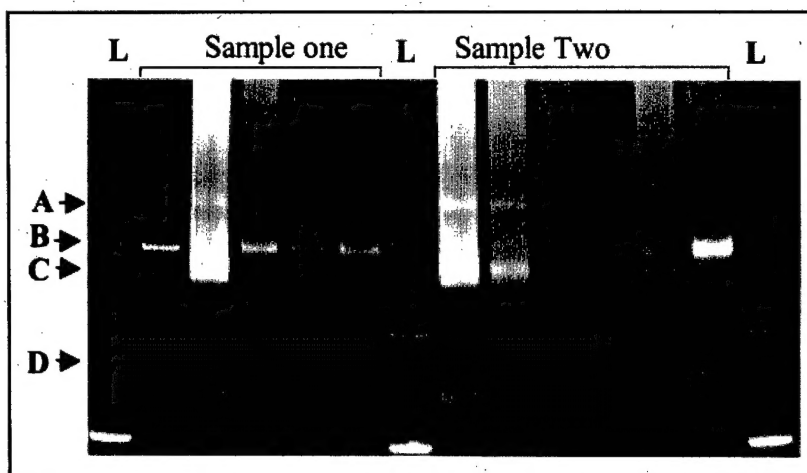


Figure 1. Detection of genes and bacteria present in dredged material. Multiplex Polymerase Chain Reaction analysis detecting A. 16S rDNA (a gene common to bacteria involved in general growth) B. NAD(P)H nitroreductase (commonly found in enteric bacteria or under nitrogen or reducing conditions). C. Dissimilatory Sulfite reductase (indicator of obligate anaerobic bacteria *Archeoglobus* and *Desulfovibrio*). D. Catechol 2,3-oxygenase (gene encoding an enzyme involved in aromatic ring cleavage). The lanes shown are analyses of dilutions of DNA extracted from sediment. L (ladder) is a size marker.

An example of this approach is demonstrated on a sediment contaminated with polynuclear aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) from New York Harbor. Polar membrane lipid fatty acid (PLFA) analysis, physiological effects of different nutrients, and the presence of different bacteria were assessed. PLFA analysis yields a quantitative measure of biomass and a profile of the types and conditions of microorganisms present. Physiological effects of different nutrients on removal of contaminants were measured in 30-percent sediment slurry microcosms. The presence of bacteria known to degrade PCBs and PAHs was examined, and showed that a high biomass of microorganisms ($\sim 5 \times 10^8$) was present. Physiological assays, PLFA, and genetic tests (Fig. 1) indicated the presence of obligate anaerobic bacteria and highly reduced contamination within the sediment. The potential of the dredged material to degrade contaminants under aerobic conditions was estimated by measuring PAH and PCB level loss after treatment in a microcosm. A loss of low molecular weight compounds (i.e., phenanthrene) relative to high molecular weight compounds was seen. High levels, at least 2×10^5 units per gram sediment, of bacteria containing genes required for cleavage of aromatic rings were found in the sediment.

Assessment of the New York Harbor dredged material suggested that the sediment may be best treated using a combination of aerobic and anaerobic regimens. Strongly reducing conditions are advantageous for degradation of highly halogenated contaminants. These contaminants can undergo

reductive dehalogenation, and the resulting dehalogenated products can then undergo aerobic degradation. Research results showed significant time and cost savings when determining appropriate treatment regimens for bench or pilot scale examinations.

Workshop at PIANC reviews worldwide innovative technologies

The U.S. Section of the International Navigation Association held its first Specialty Workshop "Innovative Dredged Sediment Decontamination and Treatment Technologies," May 2, 2000, in Oakland, Calif., as part of its annual meeting. Approximately 100 people represented the navigation industry, private consultants, environmental regulatory agencies, and academia. The purpose of the workshop was to conduct a critical review of selected technologies available for treating dredged sediments from navigation projects. In addition, the beneficial use potential for each technology was assessed.

Six invited speakers from private industry gave presentations.

Two luncheon speakers provided information on tech-

nologies used in Europe. Topics covered by the speakers were production of soil washing, flowable fill, stabilization/solidification, blended cement, glass aggregate and lightweight aggregate from decontamination, and treatment of contaminated dredged sediments. The speakers provided information on their specific technology and explained why it is unique. They also gave information about commercial availability and applicability to large-scale navigation projects. Speakers also talked about beneficial use opportunities and revenue potential from the technology. Logistical and regulatory requirements were discussed, with emphasis on preparation and utility needs as well as environmental regulatory barriers to the technology's implementation. Speakers also addressed cost and estimates. After the presentations, a technical review panel led the work-

shop in a comparative analysis of technologies and an identification of barriers to technology implementation.

Sponsors included the U.S. Section of PIANC and the U.S. Army Corps of Engineers' ERDC-WES and New York District. Cooperating organizations were the Western Dredging Association, American Association of Port Authorities, U.S. Environmental Protection Agency (Region 2), and USEPA Hazardous Substance Research Center (South/Southwest Region).

Results of the workshop will be reported in the *PIANC International Bulletin* and the *Journal of Dredging Engineering* of WEDA, and on the EOER Web site under Innovative Technology. Additional information is available from Mr. Norman Francinques at francin@wes.army.mil.

Commencement Bay, Washington, Superfund Support

Several ERDC engineers and scientists, working through CCS, are involved in EPA Superfund cleanups involving sediments. These efforts range from laboratory testing and design studies to review and oversight activities.

Two ERDC researchers participated in the Commencement Bay Sediment Management Conference, held April 25, in Tacoma, Wash., and led a follow-up

1-day seminar on contaminated sediment management and remediation for Region 10 EPA managers and staff. The focus of the Commencement Bay conference was to discuss options for the Hylebos Waterway cleanup, an operable unit of the Commencement Bay Superfund site. Options under consideration for this site include nearshore diked confined disposal facilities (CDFs), subaqueous contained aquatic

disposal (CAD) facilities, and sediment treatment. Dr. Michael R. Palermo discussed design approaches and case studies for CDF and CAD options, and Mr. Norman R. Francinques discussed the latest available information on sediment treatment approaches. For more information contact Dr. Palermo, palermum@wes.army.mil or Mr. Francinques at francin@wes.army.mil.



Dredging Products

Recently published technical notes for the DOER Program are listed below. These technical notes can be found in .pdf format at <http://www.wes.army.mil/ell/dots/doer/technote.html>.

- ERDC TN-DOER-C10 Protocols for a Rapid Clean-up/Extraction Procedure and an Improved P450RGS Dioxin Screening Assay for Sediments, March 2000
- ERDC TN- DOER-C11 Concepts and Technologies for Bioremediation in Confined Disposal Facilities, March 2000
- ERDC TN- DOER-E7 Acoustic Monitoring of Dredging-Related Suspended-Sediment Plumes, April 2000
- ERDC TN- DOER-E9 Assessment of Potential Impacts of Dredging Operations Due to Sediment Resuspension, May 2000
- ERDC TN- DOER-E10 Description of the SSFATE Numerical Modeling System, April 2000
- ERDC TN- DOER-E11 FISHFATE Users Guide: Spatially Temporally Explicit Population Simulation Model, March 2000
- ERDC TN-DOER-N6 Construction and Monitoring of a Mixed-Sediment Mound Offshore of Mobile Bay, Alabama, March 2000

Recently published technical report for the DOER Program is listed below. This technical report can be found in .pdf format at <http://www.wes.army.mil/ell/dots/doer/reports.html>.

- ERDC TR-DOER-5 Innovations in Dredging Technology: Equipment, Operations, and Management (reformatted from Corps only to public access) (3.1 meg filesize), April 2000

Recently published technical note for the EEDP program is listed below. This technical note can be found in .pdf format at <http://www.wes.army.mil/ell/dots/eedptn.html>.

- ERDC/TN EEDP-01-44 Application of Population Modeling to Evaluate Chronic Toxicity in the Estuarine Amphipod *Leptocheirus plumulosus*, April 2000

Dredging Calendar

July 9-12 - Watershed 2000, an international specialty conference sponsored by Water Environment Federation (WEF), the British Columbia Water and Waste Association, and the Western Canada Water and Wastewater Association, in Vancouver, British Columbia.

POC: msc@wef.org

July 9-12 - 17th International Conference sponsored by The Coastal Society in Portland, Ore.

July 16 - 21 - 27th International Conference on Coastal Engineering in Sydney, Australia.

POC: <http://marlin.mhl.nsw.gov.au/www/icce2000.html>

July 16-19 - Ports and Waterways (TRB) in Norfolk, VA.

POC: <http://www4.nationalacademies.org/trb/calendar.nsf>

July 31- August 4 - Annual Meeting of Universities Council on Water Resources: Living Downstream in the Next Millennium; Reconciling Watershed Concerns with Basin Management, in New Orleans, La.

POC: <http://www.uwin.siu.edu/ucowr/meeting/index.html>

August 7 - 10 - National Beach Preservation Conference in Maui, Hawaii.

POC: <http://www.soest.hawaii.edu/SEAGRANT/>

August 14 - 17 - CERF 2000 International symposium in Washington, D. C.

POC: <http://www.cerf.org/about/2000.HTM>

September 7-9 - Annual Ohio Lake Erie Conference, sponsored by Ohio Lake Erie Commission, in Sandusky, Ohio.

POC: jill.woodyard@www.epa.state.oh.us

September 11 - 14 - Oceans 2000 in Providence, R. I.

POC: <http://www.OCEANS2000.com/>

September 18 - 20 - Coastal Environment 2000 in Las Palmas, Canary Islands.

POC: <http://www.wessex.ac.uk/conferences/2000/coastal2000/>

September 18 - 22 - 22nd Consultative Meeting of the Convention on the Prevention of Marine Pollution by Dumping of Wastes and other Matter 1972 (London Convention 1972), London, UK.

September 27 - 29 - National Waterways Conference Annual Meeting in St. Louis, Mo.

POC: <http://www.waterways.org>

September 27 - 29 - Ports 2000; Second International Conference on Maritime Engineering and Ports in Barcelona, Spain.

POC: <http://www.wessex.ac.uk/conferences/2000/ports2000/>

October 14-18 - Water Environment Federation Technology (WEFTEC) 2000 Exhibition; will provide the most up-to-date information on every wastewater treatment and water quality subject. Choose workshops and technical sessions with over 500 relevant presentations — not to mention almost 100 poster presentations over the course of five days, in Anaheim, Calif.

POC: <http://www.wef.org/Weftec/index.htm>

October 15-16 - Annual Meeting of Great Lakes Commission, in Hamilton, Ontario.

POC: mdonahue@glc.org

October 17-19 - 4th State of the Lakes Ecosystem Conference (SOLEC), in Hamilton, Ontario.

POC: <http://www.epa.gov/gllindicator> or
paul.horvatin@epa.gov



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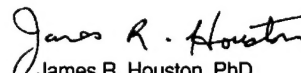
Articles for *Dredging Research* requested:

Dredging Research is an information exchange bulletin for publication of ERDC-generated dredging research results. Included are articles about applied research projects. The bulletin serves all audiences and is accessible on the World Wide Web in addition to a paper circulation of 2,800.

Articles from non-ERDC authors are solicited for publication, especially if the work described is tied to the use of ERDC-generated research results. Research articles that complement ERDC research or cover wide field applications are also accepted for consideration. Manuscripts should use a nontechnical writing style and should include suggestions for visuals and an author point of contact. Point of contact is Elke Briuer, APR, at briuer@wes.army.mil.

Dredging Research

This bulletin is published in accordance with AR 25-30 as an information dissemination function of the Environmental Laboratory of the U.S. Army Engineer Research and Development Center. The publication is part of the technology transfer mission of the Dredging Operations Technical Support (DOTS) Program and includes information about various dredging research areas. Special emphasis will be placed on articles relating to application of research results or technology to specific project needs. The contents of this bulletin are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or the approval of the use of such commercial products. Contributions are solicited from all sources and will be considered for publication. Editor is Elke Briuer, APR, briuer@wes.army.mil. Mail correspondence to the Environmental Laboratory, ATTN: DOTS, *Dredging Research*, U.S. Army Engineer Research and Development Center, Waterways Experiment Station (CEERD-EP-D), 3909 Halls Ferry Road, Vicksburg, MS 39180-6199, or call (601) 634-2349. Internet address: www.wes.army.mil/el/dots/drieb.html.


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